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15 - 18 May 2001

301/1311-7

"Miscibility & Ordering of Polymer Blends"

K. FREED
(J. Dudowicz)
University of Chicago
USA

Please note: These are preliminary notes intended for internal distribution only.

Miscibility & Ordering of Polymer Blends

- **Karl Freed & Jacek Dudowicz**
  University of Chicago

Pacifichem Dec. 16, 2000

Miscibility of molecules

- Entropy of mixing $\Delta S_{mix} \propto -\Sigma_i n_i \ln(n_i)$
- n_i is # of molecules of component i
- ΔS_{mix} often drives miscibility
- Flory-Huggins theory treats mixtures of molecules with disparate sizes ⇒
- $\Delta S_{mix} \propto -\Sigma_i n_i \ln(\phi_i)$
- ϕ_i is volume fraction of species i
- → much smaller ΔS_{mix} for polymers
- Simplest model for $\Delta E_{mix} \propto \Sigma_{ij} E_{ij} N_i N_j$
- $E_{ij} = \varepsilon_{ii} + \varepsilon_{jj} - 2\,\varepsilon_{ij}$

Flory-Huggins Theory

- Used widely to correlate diverse data
- $\Delta f^{mix}/kT = (\varphi_1/M_1)\ln \varphi_1 + (\varphi_2/M_2)\ln \varphi_2 + \chi\, \varphi_1 \varphi_2 = -\Delta s^{mix}/k + \Delta e^{mix}/kT$
- φ_i: volume fraction for type i polymers
- M_i: number of sites/chain of type i

  One parameter : $\chi \propto$ energy/kT
- Observations: χ often varies with composition, has T-indep. part, and may depend on M.
- Strong contradiction with theory

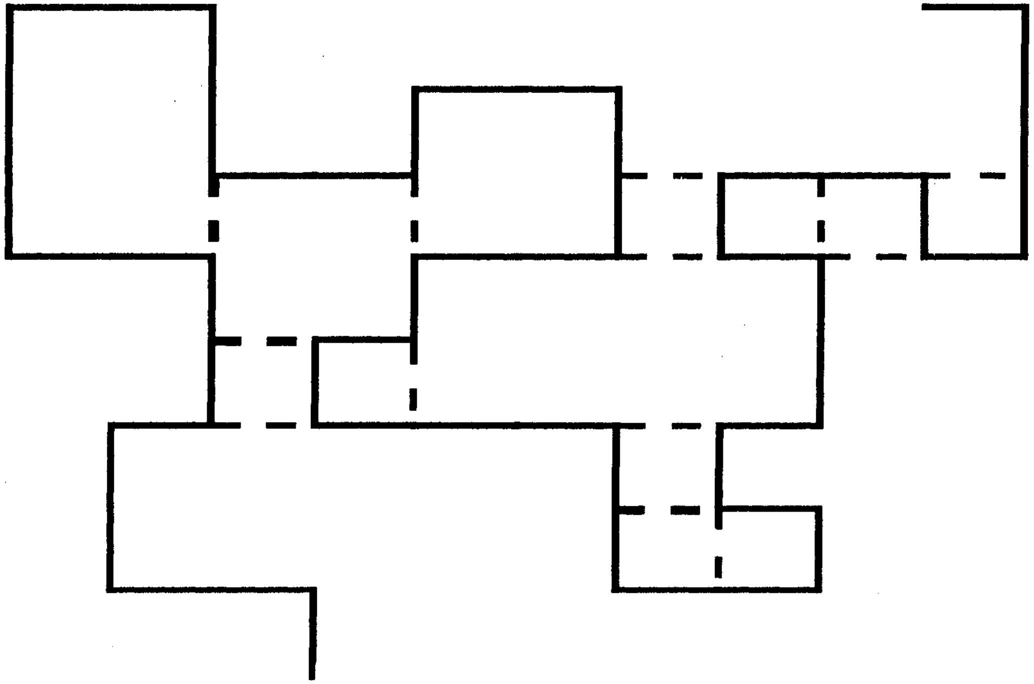
Other serious deficiencies of theory

- FH does not distinguish between linear, branch, star, graft chains
- Or copolymers of same composition (e.g., random, block, alternating)

  χ lacks molecular info as design tool
- Need relation between χ and monomer chemical structures
- Deficiency obvious by considering standard lattice model of polymers

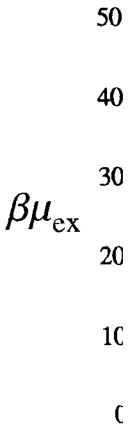
Standard lattice model of polymers

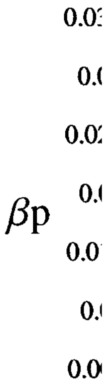
- Monomers occupy single lattice sites
- Independent of chemical species
- Ignores monomer structure



17, May, 1999

6th European Symposium on Polymer Blends: Mainz


50
40
30
$\beta\mu_{\mathrm{ex}}$
20
1


0.0
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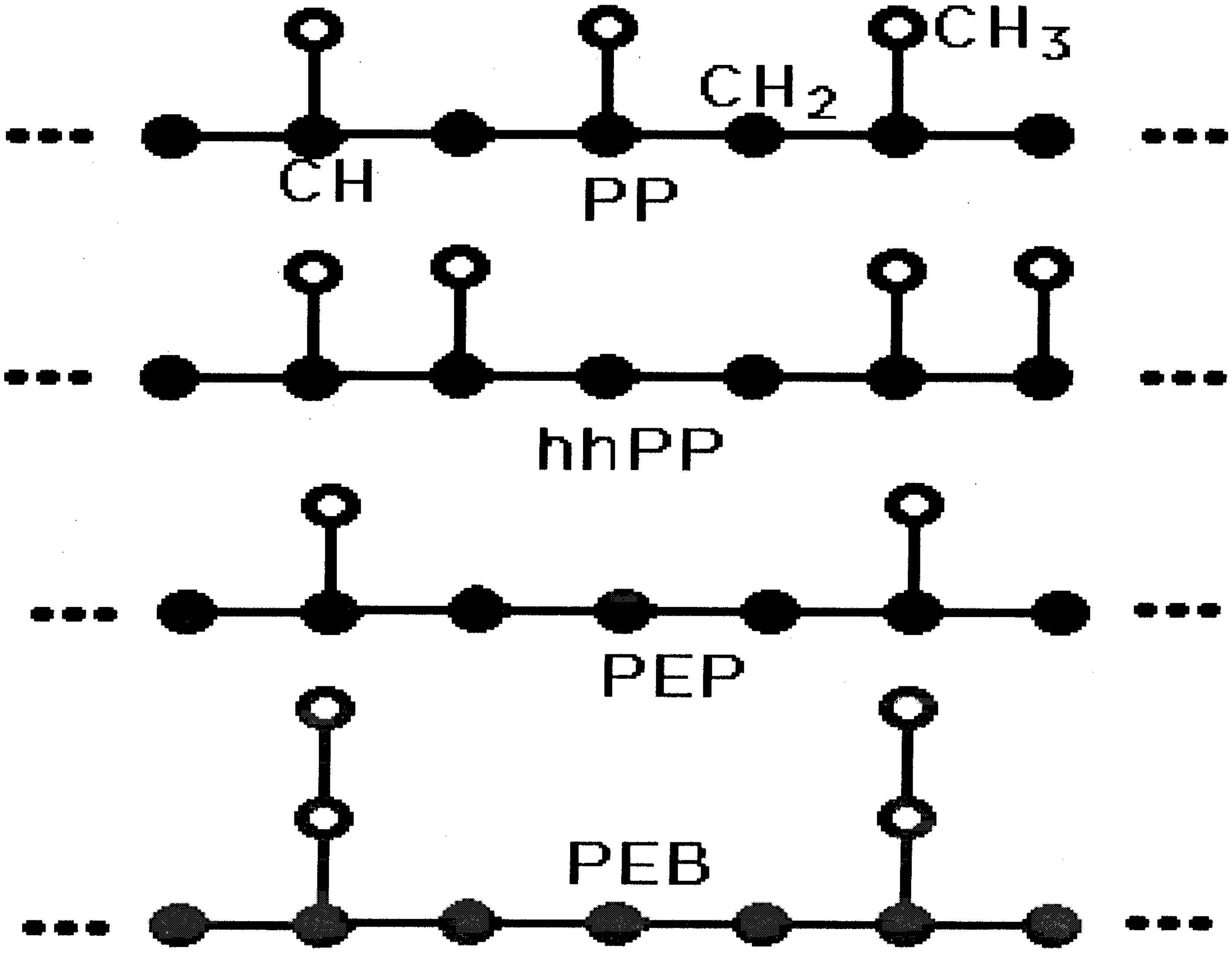
Monomer structure: Polyolefins

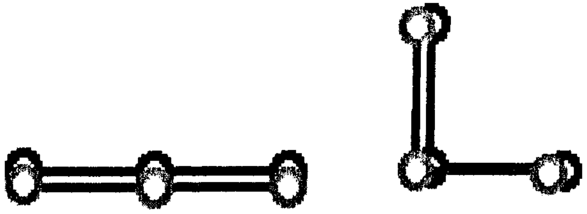


Lattice Cluster Theory (LCT)

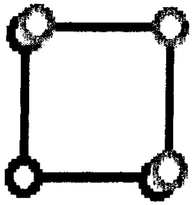
- Based on 2 fundamental advances:
  - Description of monomer structure
  - Vastly superior solution for lattice model with structured monomers
- Long list of results & predictions:
  - Explains T-indep. part of χ, along with composition, M_i, P dependence
  - Block copolymers ordering on heating
  - Monomer structure strongly affects blend miscibility:
  - Verified by many polyolefin examples

Applications of LCT: Polyolefins

- **Explain behavior with full LCT**
- **Explanation obvious using "pedestrian" LCT for M_i, $P \to \infty$**
- $\chi = [(r_1-r_2)/z]^2 + (\varepsilon/2kT)\{z-2+(2/z)[p_1(1-3\varphi_2) + p_2(1-3\varphi_1)]\} = \chi^{entropic} + \chi^{enthalpic}$
- $r_i = 1 + f_i^{tri} + 3f_i^{tetra}$



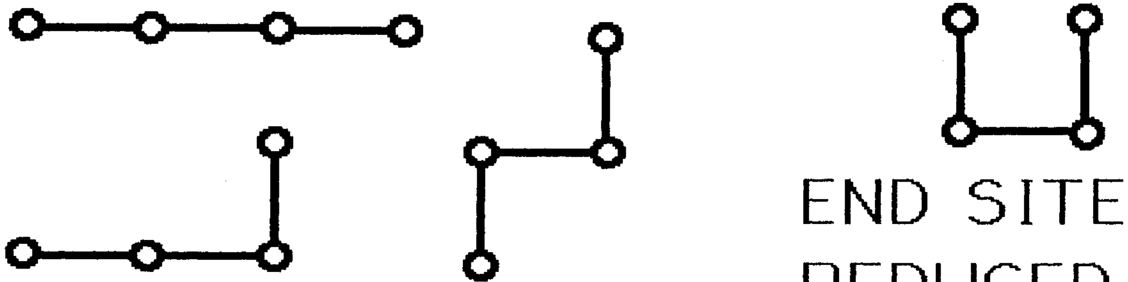
OVERLAPPING TRIMERS



OVERLAPPING TRIMER ENDS

Physical interpretation of LCT limit

- p_i depends on # of 3 bond runs
- Generalizes vague “surface fraction” concept to structured chains
- Also include chain semiflexibility
- Affects r_i and p_i
- Random copolymers: Very difficult!



ALL SITES EXPOSED
→ SURFACE FRACTION

END SITES HAVE
REDUCED SURFACE
FRACTIONS

Applications of pedestrian LCT

- Description of phase diagrams
- $kT_s(0.5)/\varepsilon = [z-2-(1/z)(p_1+p_2)]/\{(1/M_1) + (1/M_2) - [(r_1-r_2)/z]^2\}$
- Predicts LCST phase diagram: $P \rightarrow \infty$
- Explains anomalous PIB phases
- Using only a single ε !
- Explains vastly different miscibilities of PP vs. hhPP with other polyolefins
- $\Rightarrow$ can engineer blend properties by choice of monomer structures

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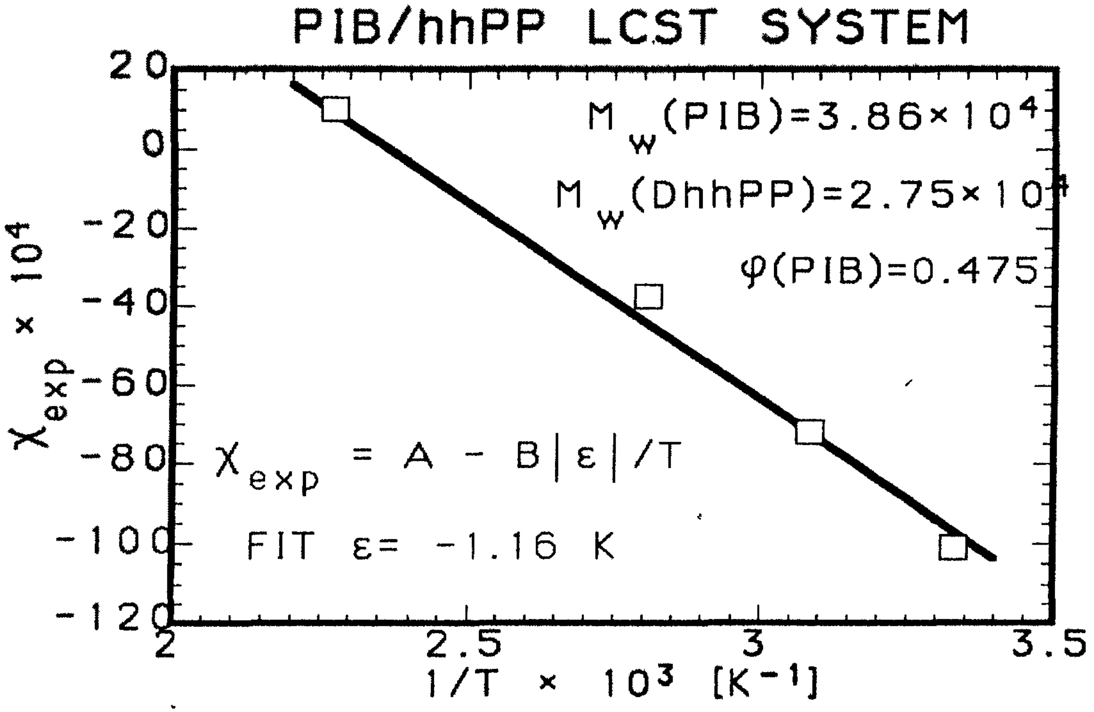
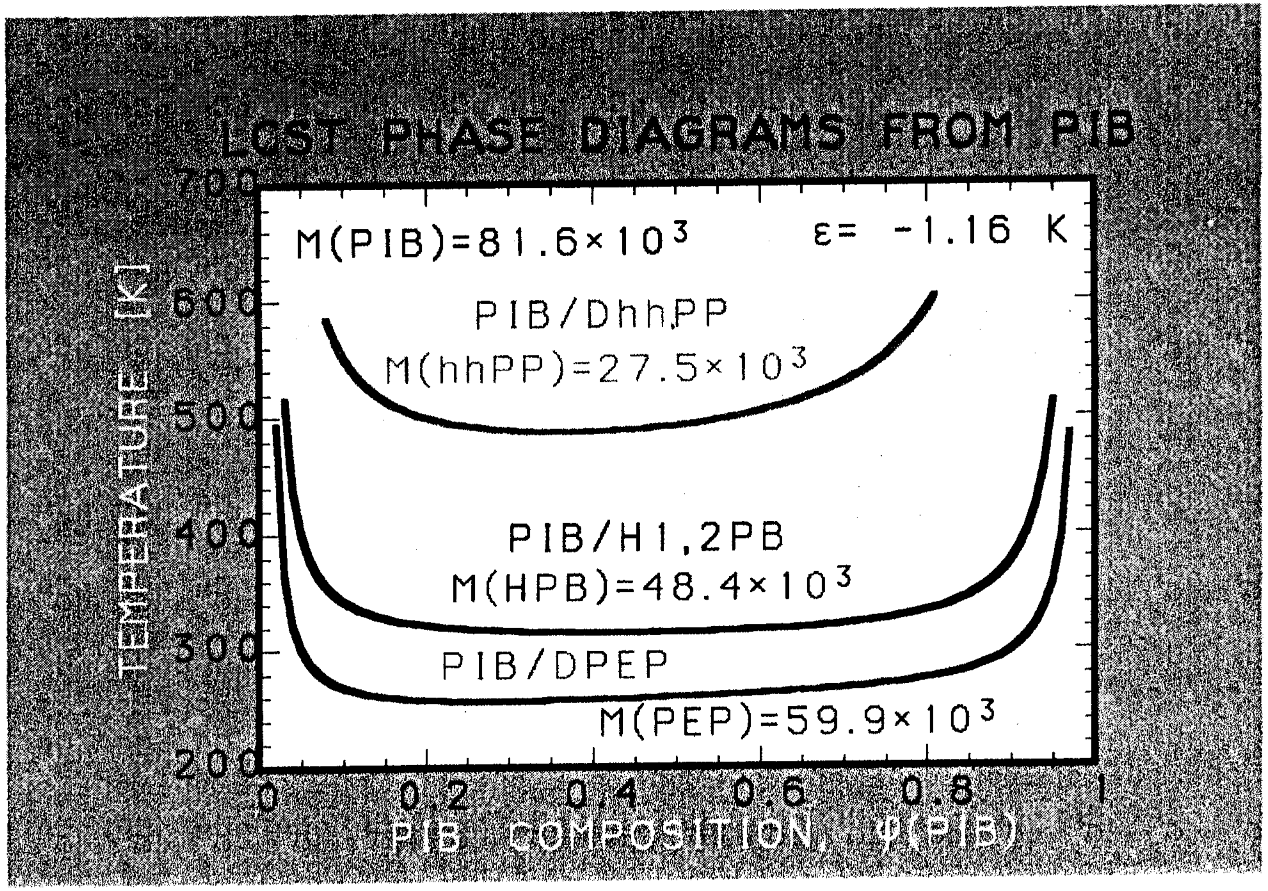
STACK:

- **Only fit ε to data; A & B from theory**
- **→ LCST for incompressible blend**
- **χ^{entropic} comes from LCT theory**
- **Now use same ε for other PIB blends**

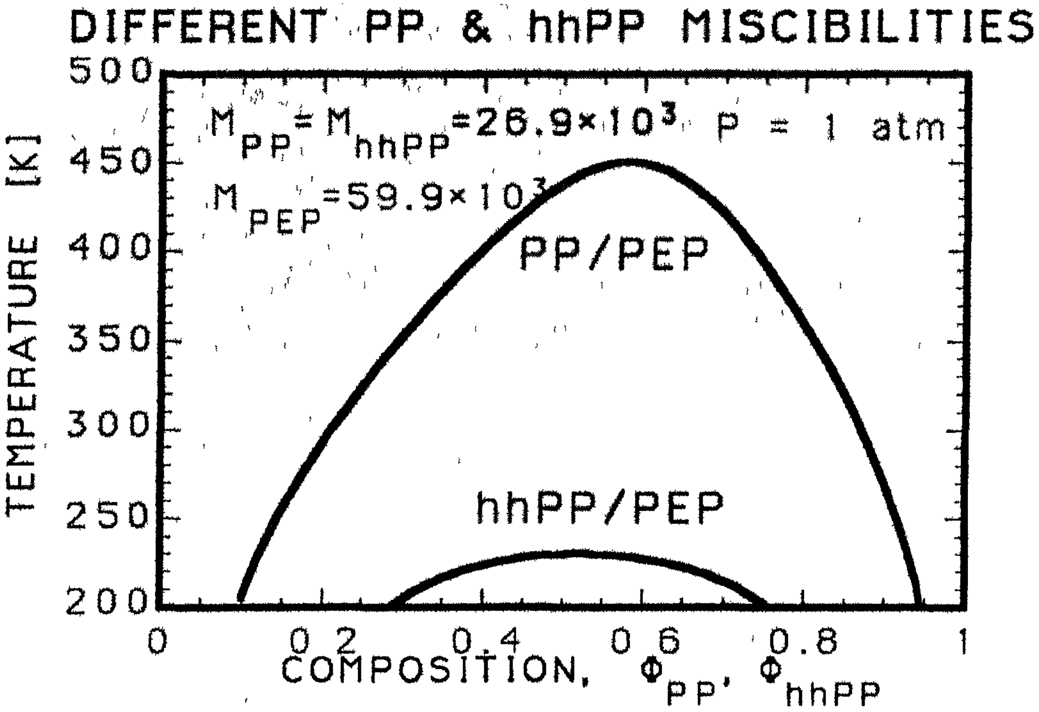


- **LCT phases for incompressible blend**
- **Use same ε for two other blends**
- **Gives T_c to within 20-30K**



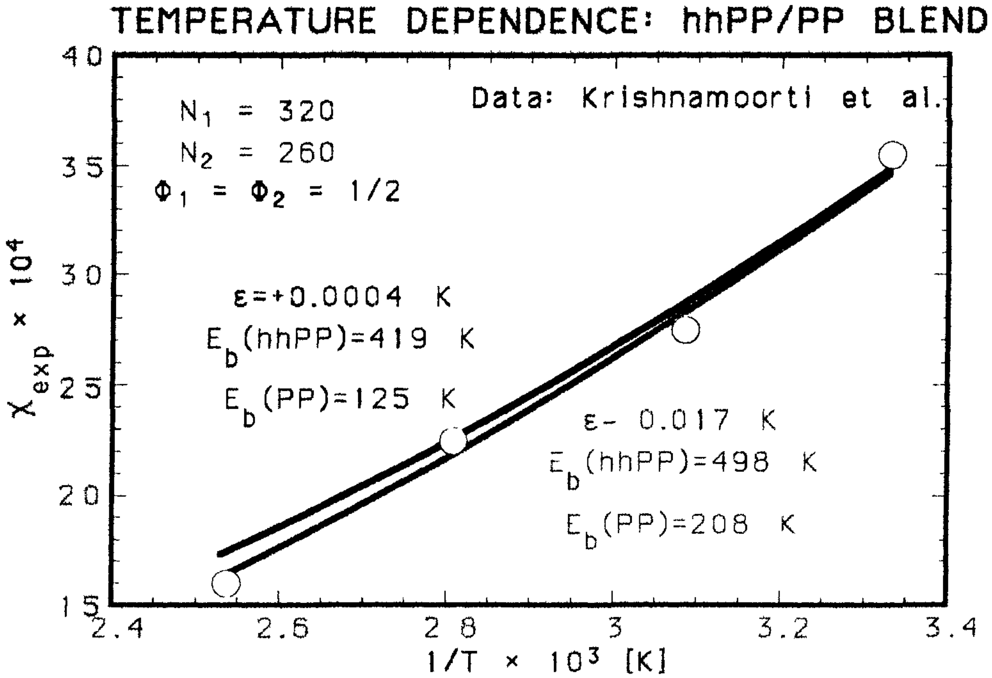
LCT for PP/PEP vs. hhPP/PEP

- **Compare using $M_{PP} = M_{hhPP}$**
- **Different surface fractions & stiffness**
- **Stiffness affects $\chi^{entropic}$**



Unusual PP/hhPP blend

- $\chi^{\text{enthalpic}} \rightarrow$ **large** ε
- χ**(PP/hhPP)** $\rightarrow$ **large negative** χ^{entropic}



“Random” Copolymers

- Theories of random copolymers
  - → Important insights into how copolymers promote miscibility
  - Based on FH counting for an assumed purely enthalpic $\chi = z(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/2kT$
  - e.g., A_x-co-$B_{(1-x)}$/A_y-co-$B_{(1-y)}$ blend:
  - $\chi = \chi_{AB}(x - y)^2$, ($\chi_{AB}$ for A/B blend)
  - Incorrect when χ contains a significant entropic portion χ_s
- Previous theories suffer from same deficiencies as FH theory

Simplified model for copolymers

- Treat as incompressible systems
- United atom models for monomers
- Include full (high M_i) LCT χ_s
  - No adjustable parameters in χ_s!
- Ignore surface fraction corrections in calculating χ_h
- ⇒ Apply FH counting for energy to united atom monomer structures
- (Surface fraction corrections more complicated to evaluate
  - → Sequence dependent contributions)

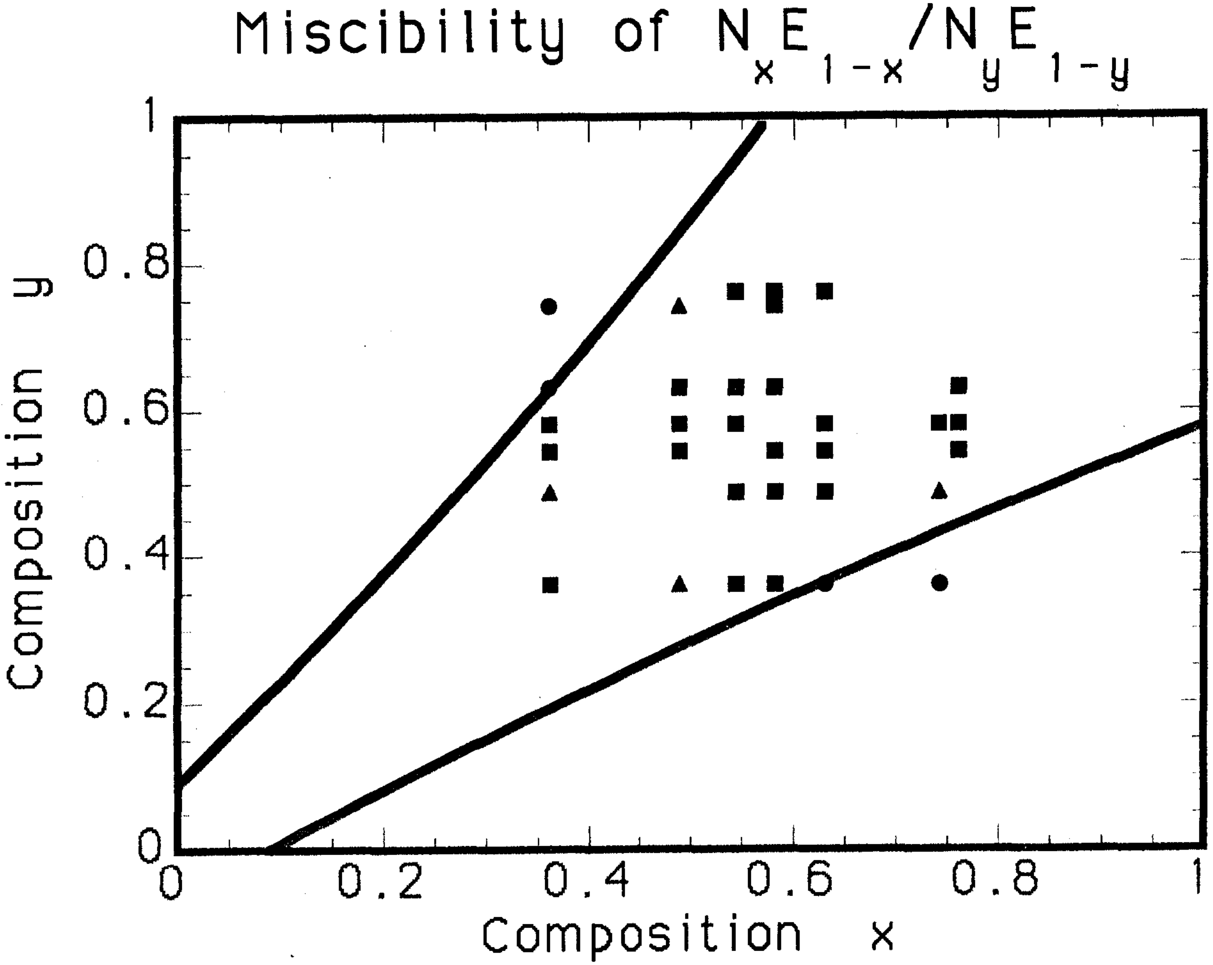
Norbornene/Ethylene Copolymers

- Norbornene: cyclic olefin

- Binary N_x-co-$E_{(1-x)}$/N_y-co-$E_{(1-y)}$ blends
- Random copolymer FH theory:
- $\Rightarrow$ Blends miscible for $|x-y| < |x-y|_c$
- Observation (MacKnight): blends are more miscible for x & y $\geq 1/2$
- Use simplified LCT copolymer theory
- Only adjustable parameter is ε
- Test various structural models:
  - Including corrections for stiffness

Norbornene/Ethylene Copolymers

- Models of binary E-co-N blends:
- a) Completely flexible chains
- b) Rigidity in norbornene side group
- c) Stiffness in N-N backbone bond
- Models b) & c) → best fits to expt.
- Entropic χ is dominant (no T dependence observed)
- Experiments: MacKnight (U Mass)


Miscibility of N_xE_{1-x}/N_yE_{1-y}
Composition y
0
0.2
0.4
0.6
0.8
1
Composition x
0
0.2
0.4
0.6
0.8
1

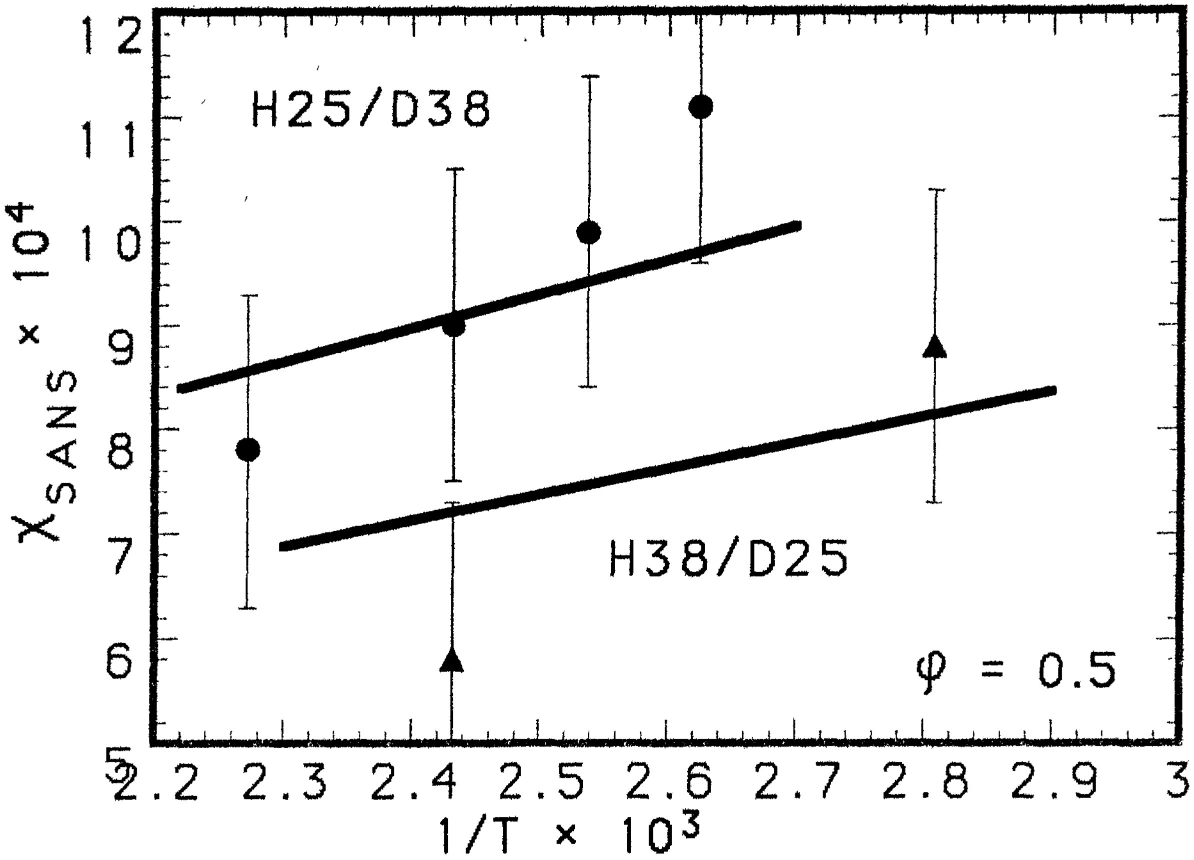
Saturated Butadiene Blends (sPB)

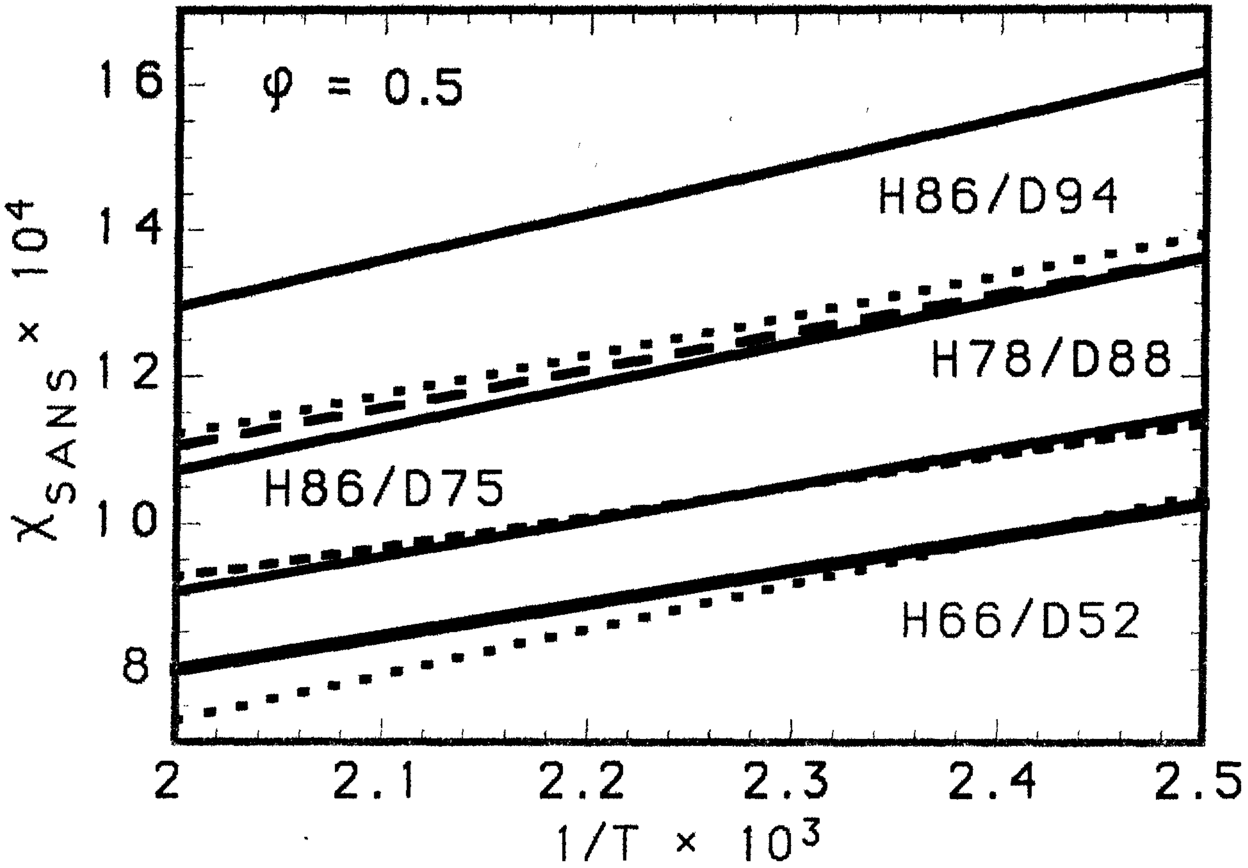
- Random copolymers due to random 1,2 & 1,4 insertions
- Binary sPB_x/sPB_y blends → simplest examples of copolymer blends
- Also most widely studied systems by SANS (Graessley-Lhose +) & nuclear reaction analysis (Klein +)
- Expt. χ vs. ϕ data agree to ± 20%
- But large difference in χ_s and χ_h ($\chi = \chi_s + \chi_h/T$)

Analysis of sPB Binary Blends

- Use same simple, easily applied theory of random copolymers
- For 23 (GL+) & 8 (K+) systems:
- Entropic χ + united atom basis FH counting for interactions
  - 2 parameters $\varepsilon_{12;12}$ & $\varepsilon_{14;14}$ for SANS
  - 3 for Klein data: also $\varepsilon_{12;14}$
  - Better fit for Klein than for SANS data
- Theory → rather small entropic χ
  - Correct deuterium swap effect
- United atom energies more realistic

Saturated polybutadienes





LCT fit to Klein data

UCST ↔ LCST: PB isotopic blends

- Hashimoto (Han): isotopic PB blends shift from UCST to LCST behavior as change microstructure!
- i.e, increase difference between x(1,2) of PBH & y(1,2) of PBD
- Random copolymer FH theory only → UCST or complete miscibility
- Use same simplified LCT as for sPB isotopic blends:
  - Explicit χ_s - no new parameters
  - χ_h from united atom model

Explanation of PS-b-PnAMA ordering

- **Again: simple, easily used theory**
  - **Incompressible system**
  - **χ same for blend & diblocks**
  - **Entropic χ from LCT (monomers)**
  - **FH-type counting of interactions between united atom groups**
- **Assume different ε for oxygen and for alkyl & aryl united atom groups**
- **→ 3 independent combinations of ε's**
- **Competition between χ_s & $\chi_h < 0$ → mechanism for lower ODT**

Results of Theory

- Main goal: Explains sign changes in enthalpic χ with variation of n
- Agree with expt.: $\chi_s > | \chi_h/T|$
- Some samples T_{ODT} sensitive to χ_s
- Predict N ranges for less sensitivity
- Predict LODT vs. UODT: n, n'$\in$ (1,12), & x of PS-b-P(nAMA$_x$-co-n'AMA$_{(1-x)}$)
- Monomer volume ratios are okay for low n, but not for $n \geq 6$